Total neutron scattering cross sections: Can we use pure MD results ?

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Definitions: $S(q,\omega)$

The Golden rule: scattered intensity [Squires 1997]

$$\frac{d^2\sigma}{d\Omega d E_f} = \frac{\sigma}{4\pi} \frac{k_f}{k_i} N S(q,\omega)$$

$$\omega = E_i - E_f$$
$$q = k_i - k_f$$

What is measured

In the nuclear data world, we use unit-less variables [Mattes 2005] :

$$S^*(\alpha,\beta) = kT\, e^{\beta/2} S(q,\omega)$$

$$\alpha = \frac{q^2 \hbar^2}{2MkT} ; \beta = \frac{-\hbar\omega}{kT}$$

$S^*(\alpha,\beta)$ is a β-symmetric function. Highly T dependent, whereas $S(q,\omega)$ evolves slowly with T (Bose factor+thermal expansion+...).

Total scattering cross section

- The integral over E_f and Ω (per molecule):

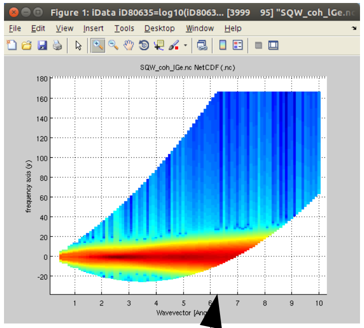
$$\sigma(E_i) = \iint \frac{d^2\sigma}{d\Omega\, dE_f}\, d\Omega\, dE_f$$

$$\ldots = \frac{\sigma_b}{2k_i^2} \iint q\, S(q,\omega)\, dq\, d\omega$$

$$E_f = E_i - \omega > 0$$

$$\cos(\theta) = \mu = \frac{k_i^2 + k_f^2 - q^2}{2 k_i k_f} \in [-1:1]$$

$$\Omega = 2\pi(1 - \cos\theta)$$

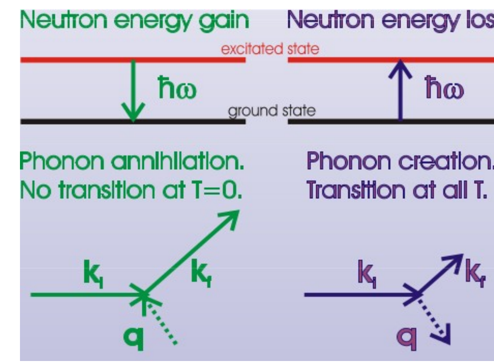


Does not depend much on the temperature.

'Dynamic range'

'quantum' $S(q,\omega)$ scattering law

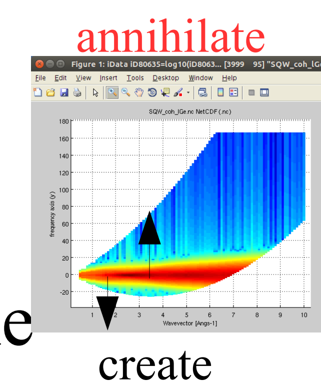
- The $S(q,\omega)$ scattering law (*aka* dynamic structure factor) is not symmetric in energy (ω). It satisfies the 'detailed balance':



$$S(q,-\omega) = e^{\overset{\beta}{-h\omega/kT}} S(q,\omega)$$

- This accounts for the temperature (entropy) and time non-reversability.

- A phonon can always be **created** from an incident neutron ($\omega < E_i$), even at T=0.



- A phonon can be **annihilated** by giving energy to the neutron, but depends on the population of phonons, with probability $e^{-h\omega/kT}$.

'Classical' $S(q,\omega)$ scattering law

- For practical reasons, we derive a symmetrical $S^*(q,\omega) = e^{-h\omega/2kT}\, S(q,\omega) = S^*(\alpha.\beta)/kT$, but other symmetric choices are possible.
- Molecular dynamics integrates atom/molecule motions over time.

$$\vec{x}_{n+1} = 2\vec{x}_n - \vec{x}_{n-1} + \vec{a}_n\,\Delta t^2$$

- The Verlet integrator used in all MD codes is *symplectic* (constant E), and is a central difference algorithm. It is *symmetric in time*.
- As a consequence, $G^*(r,t) = G^*(r,-t)$; $F^*(q,t) = F^*(q,-t)$; $S^*(q,\omega) = S^*(q,-\omega)$.

From 'classical' to 'quantum'

- For MD results and ω → -∞, the total cross section may diverge:

$$\sigma(E_i) = \frac{\sigma_b}{2k_i^2} \iint q\, e^{\frac{-\hbar\omega}{2kT}} S^*(q,\omega)\, dq\, d\omega$$

- That's because $S^*(q,\omega)$ requires a 'quantum' correction *weaker* than $e^{-h\omega/2kT}$.

- The outcome is that the S^* from MD is **not** the same quantity as the symmetrised $S^*(q,w)$ from an experiment.

- $$S(q,\omega) = \frac{2}{1+e^{-\hbar\omega/kT}} S^*_{MD}(q,\omega)$$

Frommhold (1994)
DOI: 10.1017/CBO9780511524523

Q

From 'classical' to 'quantum'

- To avoid divergence, a simple solution is to go through NJOY/LEAPR, and compute $S(\alpha,\beta)$ from a model depending on the vDOS $g(\omega)$.

σ(Ei) and S(α,β): Many Methodologies

Exp. Transmit → $\sigma(E_i)$ in liquids, powders, gases

Exp. Scatter → $S(q,\omega)$ → $S(\alpha,\beta)$ in instr. range

Exp. Scatter → gDOS(ω) → LEAPR → $S^*(\alpha,\beta)$ *legacy*

MD(*r*,*t*)+FFT → $S^*(q,\omega)$ → $S^*(\alpha,\beta)$ in rectangular extended range

MD(*r*,*t*)+FFT → vDOS(ω) → LEAPR → $S^*(\alpha,\beta)$ *Bariloche*

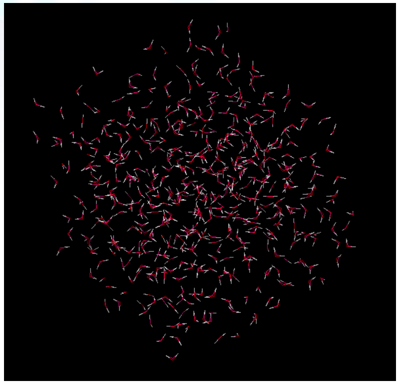
$\delta E(\delta x)+F+Dij$ → $\omega(q)$ → vDOS(ω) → LEAPR → $S^*(\alpha,\beta)$

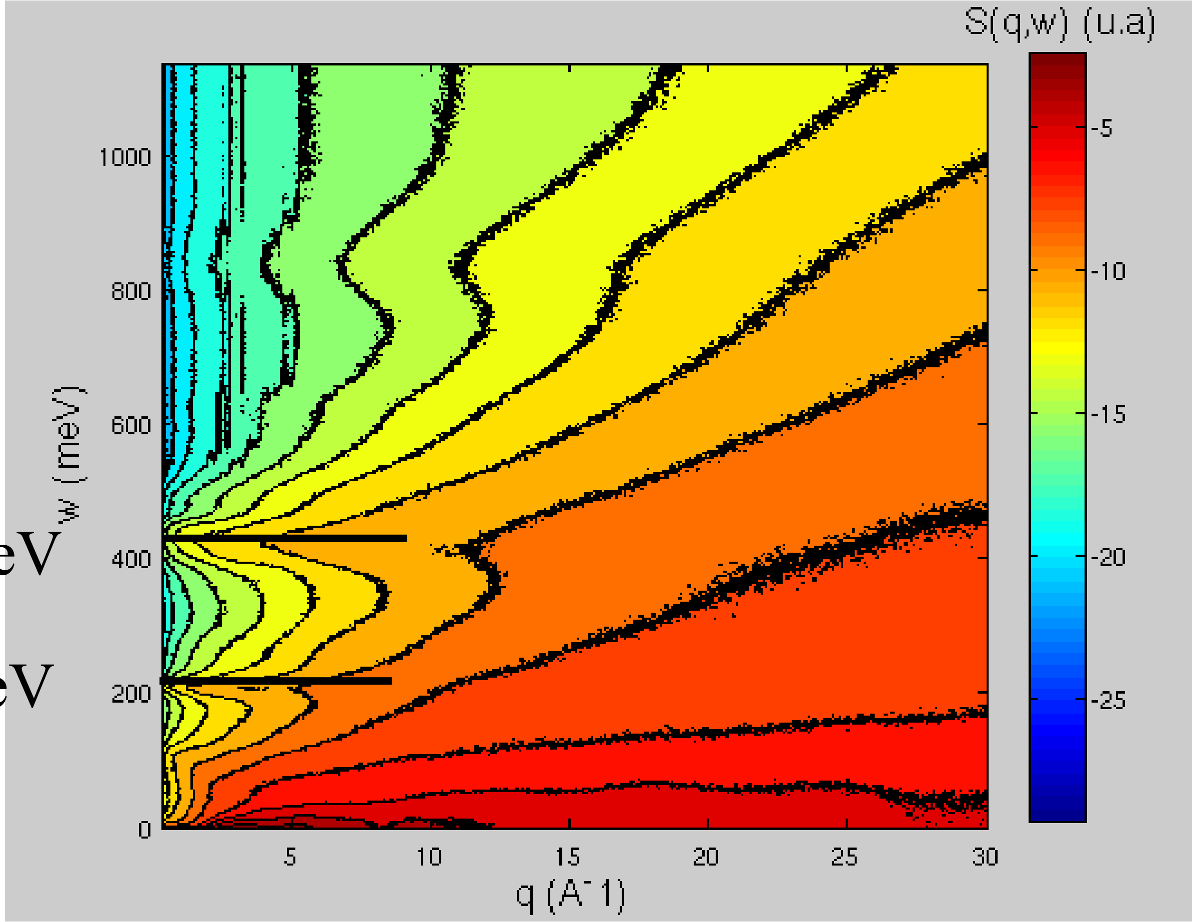
Tools

- Linux/Ubuntu system.
- GROMACS 4.6.5: MD
- nMoldyn 3.0.9 and MDANSE 1.0.0:
  - Imports PDB+DCD, generates S(q,ω)
  - https://code.ill.fr/scientific-software/mdanse
- iFit 1.8 for S(q,ω) handling
  - Symmetrise, Bosify, total XS, S(α,β), dynamic range, plotting …
  - http://ifit.mccode.org

Let's do it: GROMACS/water

512 molecules, TIP4P/2005f (based on Lennard-Jones)
10 ps as NVT, then 10 ps NVE
δt=1fs, 1e5 time steps
T=285, 310, 361, 415 K ; P=1 atm.





nMoldyn/
MDANSE

Light water

Q_{max} = 30 $Angs^{-1}$

Mattes:

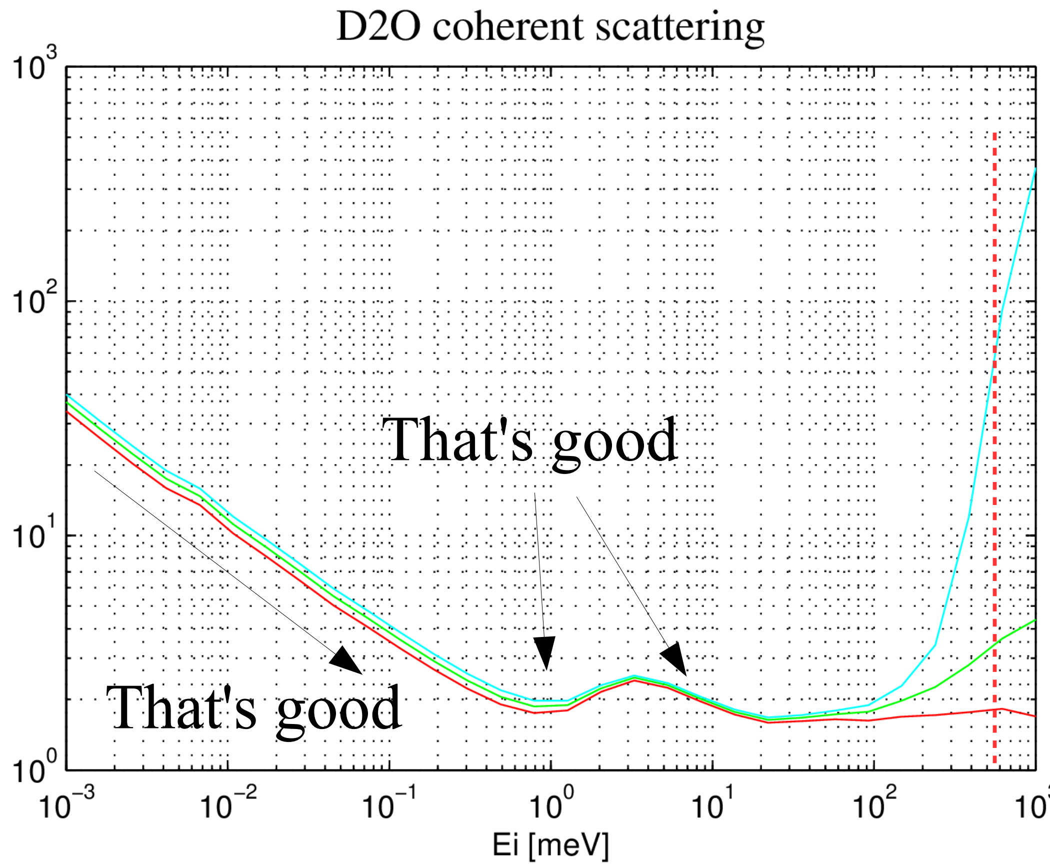
436 meV

205 meV

Application to water

Input: MD NAMD 4000 molecules, TIP3P+flexible, T=290K

$\sigma(E_i)/\sigma_b$ coherent per D2O



Quantum correction Q

Boltzmann/Schofield
$e^{h\omega/2kT}$

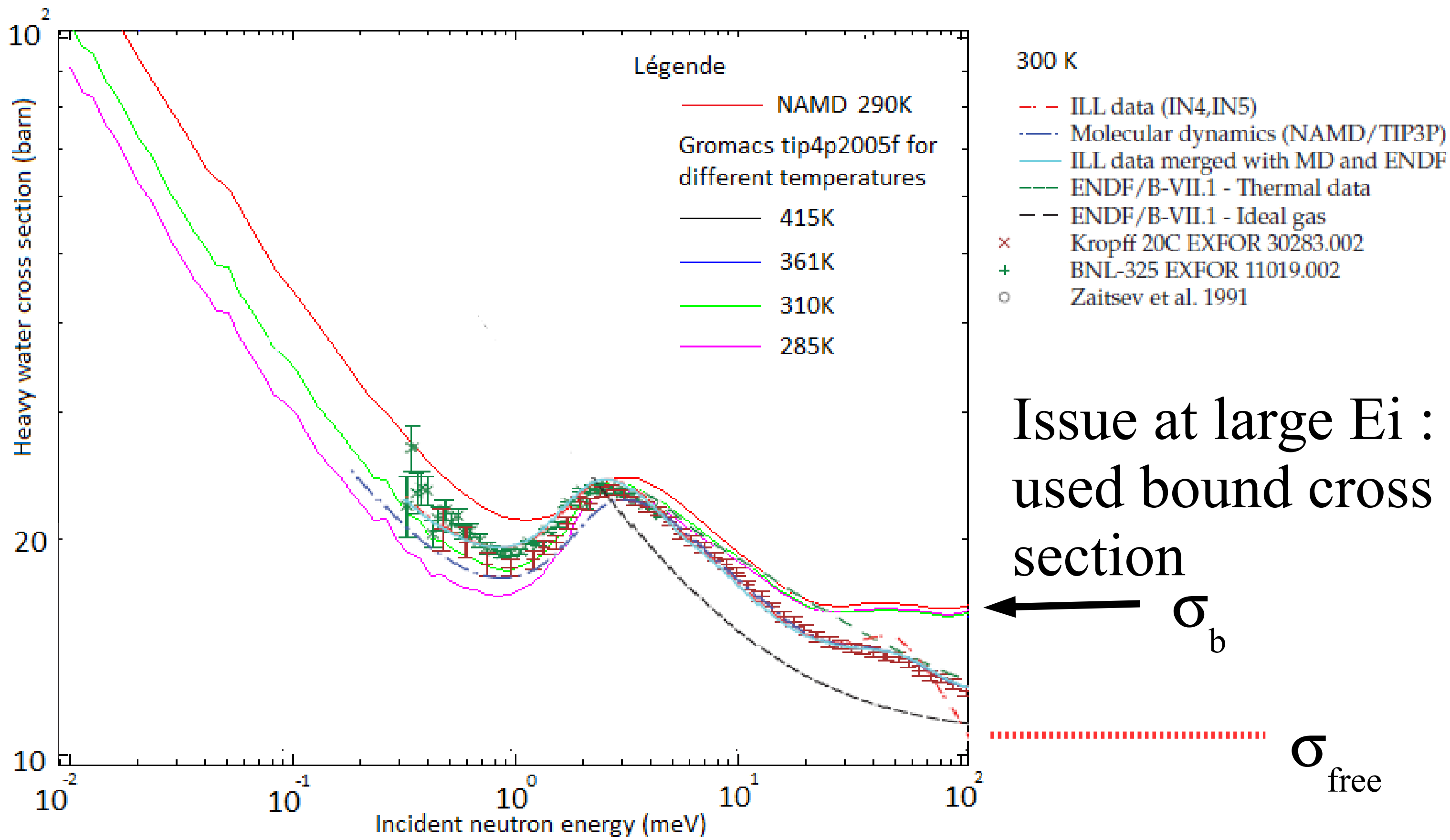
Harmonic/Bader
$h\omega/kT/(1-e^{-h\omega/kT})$

Standard/Frommhold
$2/(1+e^{-h\omega/kT})$

Q_{max}=15 Angs^{-1} → Ei_{max}=700 meV

Total σ(E_i): exp and MD

Our methodology computes σ(E_i) in absolute units. No additional correction.



Issue at large Ei : we used bound cross section

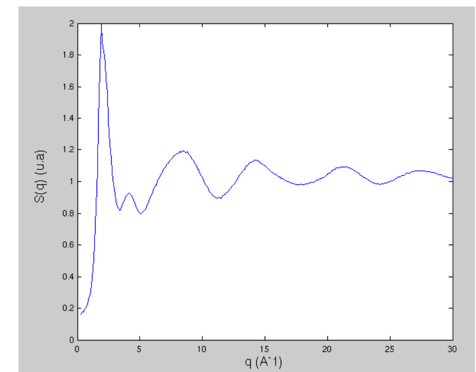
σ_b

σ_{free}

Total XS: asymptotic behaviour

- The static structure factor *S(q)* converges to 1 for q → ∞.

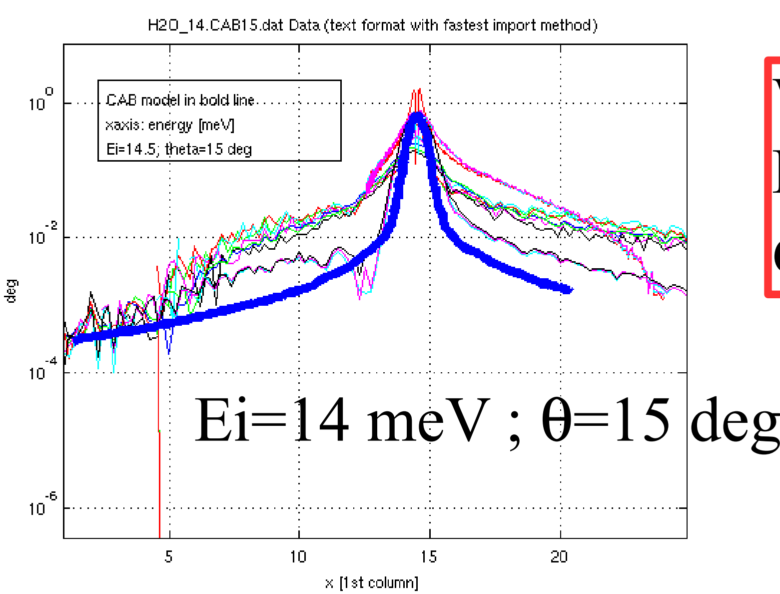
$$\sigma(E_i) = \frac{\sigma_b}{2k_i^2} \iint q S(q,\omega)\, dq\, d\omega \underset{S(q)\sim 1}{\rightarrow} \frac{\sigma_b}{2k_i^2} \int_0^{2k_i} q\, dq = \sigma_b$$



- The total scattering converges to *free* $\sigma_{coh}+\sigma_{inc}$.
- We used σ_b as pre-factor. Must go continuously from σ_b (cold-thermal) to σ_{free} (at large Ei).

Next steps

- Integrate experimental data sets
- Properly handle multiple scattering in experiments.
- Compute gDOS to compare with Bellisent-Funel and vDOS.
- Compute S(θ,ω) to compare with Bischoff et al.



WARNING:
Raw data !
ω up to 400 meV